

where the shear constant s , defined as change of reduced viscosity with velocity gradient, is seen to be

$$s = (3l\eta/gr)k \quad (25)$$

Summary

1. The Wilberforce equation, which includes kinetic energy and end effect corrections for capillary viscometers, can be rearranged to an equation in which apparent fluidity is linear in driving pressure. An additional term, also linear in pressure, is produced by drainage errors. A

method is described for the experimental evaluation of these corrections.

2. Polystyrene and polyvinylpyridine solutions exhibit a fluidity which varies linearly with pressure, after the above corrections have been made. This residual variation is ascribed to a distortion and/or orientation of the polymer molecule. Analysis of the data permits description of the shear dependence in terms of a single arbitrary constant k , the shear constant. At a pressure p , the intrinsic viscosity of a polymer is

$$[\eta]_{\infty}(1 - kp)$$

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Bolaform Electrolytes. I. Di-(β -trimethylammonium Ethyl) Succinate Dibromide and Related Compounds¹

BY RAYMOND M. FUOSS AND DAVID EDELSON²

Introduction

We have been investigating the properties of polyelectrolytes³ of the chain type and found it desirable to synthesize multivalent electrolytes of the same general structure, but of much lower molecular weight. For example, conductance data on the methyl bromide addition compound of the polyester obtained by condensing succinic anhydride and methyldiethanolamine⁴ needed for their interpretation the limiting conductance of the monomer unit. Two general types of fundamental units could be considered, which may be represented schematically as



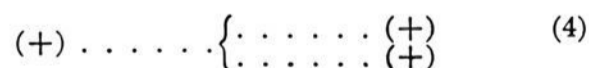
and



In (1), we have a charged group at the center of a chain of atoms; in (2) we have a chain of atoms connecting two charged atoms. An example is shown in Fig. 1, which is a photograph of the Hirschfelder model of the di-(β -trimethylammonium-ethyl) sebacate ion. For the latter type, we propose the name⁵ "bolaform" electrolytes; by extension of the meaning, we shall use the term to designate multivalent electrolytes of low molecular weight, e.g., structures such as



and



In addition to their bearing on the polyelectrolyte problem, bolaform electrolytes show promise of

being useful in understanding the behavior of multivalent simple ions. The calcium ion, for example, may be considered in an approximate sort of way as the limit of structure (2) as the chain of connecting ions shrinks to zero, and the lanthanum ion as the corresponding limit of structures (3) and (4). In other words, we hope to arrive at a better understanding of some of the peculiarities of multivalent ions by studying the properties of bolaform electrolytes and extrapolating to zero chain length.

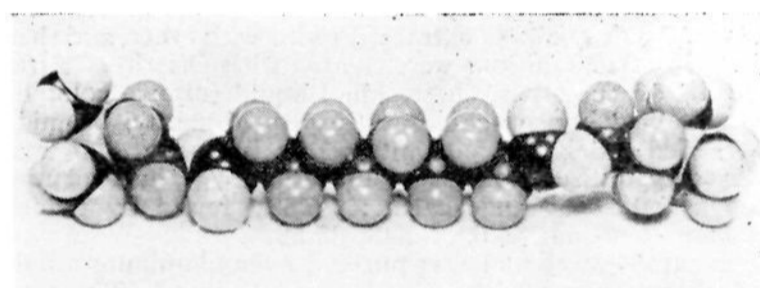
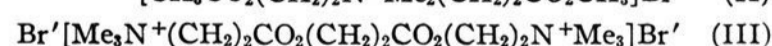
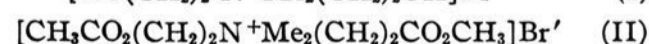


Fig. 1.—Hirschfelder model of di-(β -trimethylammonium-ethyl) sebacate ion.

In this paper, we present conductance data on two salts (I and II) of structure (1) and on one bolaform electrolyte (III) of structure (2). Data on other bolaform electrolytes⁶ will be presented soon. These salts have the structures



Salts I and II behave like typical 1-1 electrolytes with large cations, while Salt III exhibits a behavior resembling that of 2-1 electrolytes. An analysis of the conductance curves of Salt III in methanol, in ethanol and in a mixture of these solvents shows that one anion is essentially free while the other is in association equilibrium⁷ with the singly charged aggregate $(-)(+)\dots\dots(+)$.

(6) Victor F. Chu, Thesis, Yale University, 1950.

(7) R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

(1) Office of Naval Research, Project NR 054-002; Paper No. 26.

(2) Results herewith presented were abstracted from a thesis presented by David Edelson to the Graduate School of Yale University, June, 1949, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry.

(3) R. M. Fuoss, *Science*, **103**, 545 (1948).

(4) R. M. Fuoss and D. Edelson, *J. Polymer Sci.*, **5**, S33 (1950).

(5) "bola, a kind of missile weapon consisting of balls of iron, stone, etc., attached to the ends of a thong or cord A third ball is sometimes attached to a cord nearly half as long as the main cord and at a point bisecting it." "Webster's New International Dictionary," Second Edition, Merriam Co., Springfield, Mass., 1938, p. 303.

Experimental

Materials. *N,N*-Dimethyl-*N,N*-di- β -ethanolammonium bromide (Salt I) was prepared by distilling 10 g. of methyl bromide into a chilled mixture of 7 ml. of methyldiethanolamine and 3 ml. of ethanol. The tube was sealed and taken from the cold bath; at about 15°, an exothermic reaction set in, heating the tube to about 60°. After several minutes, the contents separated into two liquid phases. After allowing the excess methyl bromide to evaporate, the concentrated alcoholic solution was chilled in an ice-bath. The crystals which separated were centrifuged, and twice recrystallized from *n*-propanol (*ca.* 1 ml./g. salt). The salt was washed with dioxane and dried in vacuum at 40°. It is extremely deliquescent, and was stored in a desiccator. The salt begins to decompose above 200° and liquefies around 250°. *Anal.* Calcd.: Br', 37.33%; found by potentiometric titration: Br', 37.30, 37.35

N,N-Dimethyl-*N,N*-di- β -acetoxethylammonium Bromide (Salt II).—Methyldiethanolamine was refluxed for 1 hour with an excess of acetic anhydride. The unreacted anhydride and the acetic acid formed were then distilled off, and the ester purified by fractional distillation; b.p. 251°. It was dissolved in cold anhydrous dioxane and an excess of cold methyl bromide was added. The mixture was allowed to reflux at room temperature under a Dry Ice condenser for 1 hour, during which time the quaternary salt precipitated. The salt was twice recrystallized from anhydrous *n*-propanol (*ca.* 2 cc./g.; cooling to -20° was necessary to start crystallization), washed with dioxane and vacuum dried at 40°. Salt II is also very deliquescent. Bromide was determined by potentiometric titration. Calcd., 26.80; found, 26.80, 26.70.

Di-(β -trimethylammonium-ethyl) Succinate Dibromide (Salt III).—The parent ester was prepared by ester interchange between dimethylaminoethanol and diethyl succinate by Sickels⁸ procedure. A solution of 0.2 g. of sodium in 75 ml. (0.75 mole) of dimethylaminoethanol was prepared and 12 ml. (0.067 mole) of diethyl succinate was added. The mixture was allowed to stand for 24 hr., protected by a drying tube, and then was refluxed (oil-bath at 165°) for 10 hr.; during this time, 5.2 ml. (*vs.* 6.2 ml. calcd.) of ethanol was collected. The excess dimethylaminoethanol was then removed at 59° and 42 mm. The still residue was taken up in ether, and washed once with water. The water was extracted twice with ether, and then combined ether solutions were treated with Drierite. After distilling off the ether, the residual liquid (orange colored) was dissolved in acetone and an excess of methyl bromide was added. Salt III precipitated as it formed. It was twice recrystallized from ethanol (*ca.* 30 cc./g.) and vacuum dried at 40°. Bromide calcd.: 35.50; found by potentiometric titration, 35.60, 35.43, 35.52.

Solvents.—Methanol was purified over aluminum amalgam, as recommended by Hartley and Raikes.⁹ The conductance was $0.1-0.2 \times 10^{-6}$. The density at 25.00° was found to be 0.78652. The dielectric constant¹⁰ was 31.5 and the viscosity¹¹ 0.005465. Ethanol was refluxed over sodium-lead alloy (Hydrone) for 4 hr. and then over freshly activated aluminum oxide, previously heated at 210° for 12 hr. It was then distilled; $78.2 \pm 0.05^\circ$ at 773 mm. The density at 25.00° was 0.78567; conductance, 0.04×10^{-6} ; viscosity¹¹ at 24.67°, 0.01105; dielectric constant¹⁰ 24.3. A mixture of 518 g. of purified methanol and 321 g. of purified ethanol was also used as a solvent for Salt III; mole fraction methanol, 0.698; conductance, 0.145×10^{-6} ; density at 25.00°, 0.78603; viscosity¹¹ at 24.67°, 0.006868; dielectric constant at 25.00°, 28.0. Dielectric constants of the solvents were measured on a Wheatstone bridge in a calibrated cell of the type described by Mead and Fuoss.¹² Viscosities were measured on a Bingham¹³ viscometer.

Technique.—Conductances were measured on a Shedlovsky bridge¹⁴ using cells with constants 0.20660 and 0.05277. The electrodes were left unplatinized in order to minimize

adsorption errors. Polarization errors (maximum, 0.3%) were eliminated by extrapolating to infinite frequency.¹⁶ Stock solutions were prepared in weight burets; salts were dried to constant weight in a miniature vacuum oven. Solvent was weighed into the clean dry cell, and its conductance was measured. Then a portion of stock solution was added, sufficient to give a cell resistance of the order of 1000 ohms. After measuring this solution, more solvent was weighed in. All runs were made by dilution, because adsorption errors were found to be negligible with this procedure. When the cell became too full, a weighed amount of solution was removed, and then further portions of solvent were weighed in. The conductance measurements were made at $25.00 \pm 0.02^\circ$.

Results

The experimental data are summarized in Tables I–III, where *c* is equivalents of bromide per liter and Λ is equivalent conductance, 1000 κ/c .

TABLE I
CONDUCTANCES IN METHANOL

Salt I		Salt II		Salt III	
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
1.029	100.50	1.633	95.41	0.722	115.56
1.474	99.83	2.483	94.43	1.147	114.36
1.843	99.47	3.526	93.95	1.599	112.71
2.333	98.92	4.932	93.07	2.369	110.37
3.110	98.23	6.634	92.11	3.481	108.06
4.104	97.42	9.221	90.99	4.704	105.40
5.926	95.89	11.344	90.12	6.437	102.41
		13.960	89.14	9.210	98.72
		16.211	88.30	14.081	93.89
		21.005	86.71	18.116	90.73

TABLE II
CONDUCTANCE OF SALT III IN ETHANOL

Series 1		Series 2	
$10^4 c$	Λ	$10^4 c$	Λ
1.263	41.70	0.1503	48.82
1.791	39.47	.2136	48.09
2.740	36.59	.3003	47.15
4.209	33.61	.4757	46.02
5.486	31.76	.9461	42.73
7.055	30.03	1.3240	40.78
9.095	28.37	1.9670	38.25
12.037	26.59		

TABLE III
CONDUCTANCE OF SALT III IN MIXED SOLVENT

$10^4 c$	Λ	$10^4 c$	Λ
0.8816	85.73	5.467	74.68
1.259	84.46	7.995	70.89
1.661	83.21	10.852	67.80
2.201	81.63	15.085	64.19
3.276	78.90	20.508	60.87

Discussion

The conductance curves for the three salts in methanol are shown in Fig. 2. The points for Salt II lie almost on the limiting tangent; the small negative deviations indicate a slight pairwise association of anions and cations. Salt I exhibits a stronger downward curvature, corresponding to a greater degree of association; as will be seen later, we ascribe this effect to the presence of the unmasked hydroxyl groups in the cation of Salt I. Salt III, on the other hand, has a conductance curve with a distinct inflection point, and approach to the limiting tangent does not appear until

(8) J. P. Sickels, Thesis, Yale University, 1939.
 (9) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).
 (10) G. Akerlöf, *THIS JOURNAL*, **54**, 4125 (1932).
 (11) W. N. Maclay, Thesis, Yale University, 1950.
 (12) D. J. Mead and R. M. Fuoss, *THIS JOURNAL*, **61**, 2047 (1939).
 (13) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.
 (14) T. Shedlovsky, *THIS JOURNAL*, **52**, 1793 (1930).

(15) G. Jones and S. M. Christian, *ibid.*, **57**, 272 (1935).

extreme dilutions. We therefore conclude that considerable association occurs in Salt III in our working range of concentration. These qualitative descriptive statements are based on an analysis of the data, which will be presented next.

Using Birge's¹⁶ values for universal constants, Onsager's¹⁷ equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \quad (5)$$

becomes at 25.00° for 1-1 electrolytes

$$\Lambda = \Lambda_0 - (159.37 \Lambda_0/D)^{1/2} + 4.777/\eta D^{1/2} \sqrt{c} \quad (6)$$

for a solvent of dielectric constant D and viscosity η . Here c is concentration in equivalents per liter. For methanol, with $D = 31.5$ and $\eta = 0.005465$

$$\Lambda = \Lambda_0 - (0.901 \Lambda_0 + 155.5)\sqrt{c} \quad (6')$$

represents the limiting tangent to the curve. At finite concentrations, the conductance is lower than that given by Eq. (5), due to neglect of higher terms in the mobility equation; in many solvents, a further decrease due to ion association⁷ occurs. Using Shedlovsky's¹⁸ method of extrapolation, we obtain for Salt I in methanol, $\Lambda_0 = 103.2$ and $K = 0.030$ and for Salt II in methanol, $\Lambda_0 = 98.6$ and $K = 0.089$.

These constants may be directly correlated with the structure of the cations of Salts I and II. Each carries dipolar groups (two hydroxyls in I and two acetoxy groups in II) whose fields add to that of the corresponding central nitrogen atom of the cation. The conductances of tetramethylammonium bromide¹⁹ and of tetraethylammonium bromide²⁰ have also been measured in methanol; applying the extrapolation method¹⁸ to these data, we find for Me_4NBr in methanol, $\Lambda_0 = 125.3$ and $K = 0.033$ and for Et_4NBr in methanol, $\Lambda_0 = 117.0$ and $K = 0.034$. If size²¹ of cation were the only variable to consider, we would expect Salt I to have limiting conductance and dissociation constant about the same as those of Et_4NBr (which also has eight atoms around the central nitrogen); actually we find a considerably smaller Λ_0 but about the same K . The smaller mobility probably means solvation of the cation due to hydrogen bonding between the hydroxyls on it and in the solvent²² which results in an effectively larger hydrodynamic unit. Fairly stable solvation is also indicated by the approximate equality of the K 's for Salt I, Me_4NBr and Et_4NBr ; in non-solvating solvents, insertion of a hydroxyl into a quaternary ion has a marked effect on K . Thus, ethyltrimethylammonium picrate has $K = 44.0 \times 10^{-3}$ in nitrobenzene²³ and $K = 4.60 \times 10^{-5}$ in ethylene dichloride²⁴ while hydroxyethyltrimethylammonium picrate has $K = 7.0 \times 10^{-3}$ and 0.66×10^{-5} , respectively, in these solvents, *i.e.*, a

(16) R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(17) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(18) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, *THIS JOURNAL*, **71**, 1496 (1949).

(19) T. H. Mead, O. L. Hughes and H. Hartley, *J. Chem. Soc.*, 1207 (1933).

(20) A. Unmack, E. Bullock, D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc. (London)*, **A132**, 427 (1931).

(21) H. L. Pickering and C. A. Kraus, *THIS JOURNAL*, **71**, 3288 (1949).

(22) H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

(23) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947).

(24) D. J. Mead, J. B. Ramsey, D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **69**, 528 (1947).

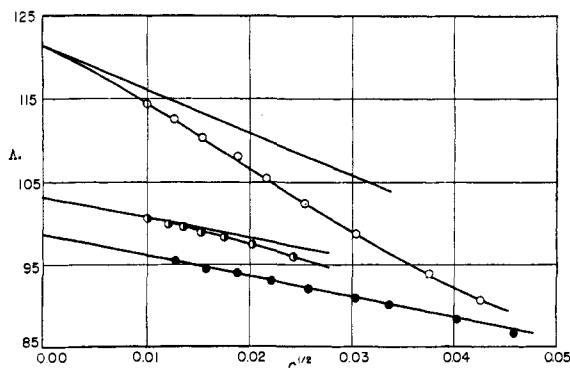


Fig. 2.—Conductance curves in methanol: open circles, Salt III; half-black, Salt I; solid black, Salt II.

decrease to about one-seventh. (Absence of solvation in these solvents is indicated by the limiting conductances; replacement of a hydrogen atom in the ethyl group by a hydroxyl has only a very small effect on Λ_0 in nitrobenzene and in ethylene dichloride, in contrast to the large effect in methanol.)

If, now, we consider the data for Salt II, we find a decrease in Λ_0 compared to Salt I, corresponding to the added bulk of the acetoxy groups. The striking effect, however, is the threefold increase in K . Salt II is only slightly associated, as is obvious in Fig. 2. We conclude that the orientation of the dipoles in the cation of Salt II is such that their field opposes that of the central nitrogen, thus decreasing the attraction for anions. A similar effect was observed in ethylene dichloride²⁴: $K = 6.6 \times 10^{-6}$ for choline picrate and 19.6×10^{-6} for acetylcholine picrate, *i.e.*, an increase of threefold for acylating one hydroxyl. In going from Salt I to Salt II, two hydroxyls are acylated; methanol has a considerably higher dielectric constant than ethylene dichloride, however, and the electrostatic effects are naturally weaker. The behavior of the two systems is, nevertheless, closely parallel.

We now turn to a consideration of Salt III, the 2-1 electrolyte. The Onsager equation becomes

$$\Lambda = \Lambda_0 - \left\{ 6.86 \times 10^6 \frac{\Lambda_0}{(DT)^{3/2}} \frac{q^*}{1 + \sqrt{q^*}} + \frac{151.6}{\eta(DT)^{1/2}} \right\} \sqrt{c} \quad (7)$$

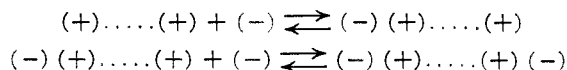
where

$$q^* = 2/3(1 + \lambda_a^0/\Lambda_0) \quad (8)$$

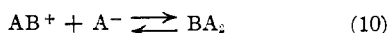
Here c is concentration of (monovalent) anion in equivalents per liter, λ_a^0 is anion equivalent conductance and $\Lambda = 1000 \kappa/c$. Hartley^{20,25} gives $\lambda_a^0 = 55.5$ in methanol at 25°. A free hand extrapolation of the $\Lambda-\sqrt{c}$ plot gave the preliminary value $\Lambda_0 = 122.2$ for Salt III in methanol. It will be observed in Fig. 2 that the data for Salt III approximate linearity with a slope considerably greater than that calculated by Eq. (7). We therefore suspect that there is an inflection point in the conductance curve near $\sqrt{c} = 0.02$, due to ion association (which produces a concave-up $\Lambda-\sqrt{c}$ curve) and that the curve becomes concave-

(25) J. E. Frazer and H. Hartley, *Proc. Roy. Soc. (London)*, **109A**, 351 (1925); A. Unmack, D. M. Murray-Rust and H. Hartley, *ibid.*, **127A**, 228 (1930).

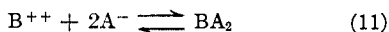
down at lower concentrations, in order to reach $\Lambda = \Lambda_0$ at $c = 0$ with the theoretical slope. Salt III can associate in the stages



For abbreviation, we write the above as



where A stands for the anion and B for the divalent cation. A combination of (9) and (10) leads, of course, to



One might attempt to describe the conductance curve on the basis of either (11) or (9) and (10). Calculation shows that the termolecular reaction (11) does not fit the data at all. For (9) and (10), we may write the formal dissociation equations

$$k_1 = [A^-][AB^+]/f_A f_{AB}/[BA_2] f_{A_2B} \quad (12)$$

and

$$k_2 = [A^-][B^{++}]/f_A f_B/[AB^+] f_{AB} \quad (13)$$

where k_1 and k_2 are reciprocal association constants describing reactions (9) and (10). The quantities in brackets indicate molar concentrations of the corresponding species, and the f 's are activity coefficients. This association is assumed to be due solely to the influence of coulomb forces⁷; by hypothesis, no covalent bonds are involved. The data were compared with Equations (12) and (13); it was found that an adequate limiting description of the behavior of Salt III could be obtained on the basis of the assumptions: $k_2 \neq 0$, $k_1 \gg k_2$. That is, we assume negligible association to give electrically neutral BA_2 structures and a certain amount of pairwise association of B^{++} ions with anions to give singly charged AB^+ ions.

The analysis is as follows. The stoichiometric equivalent concentration c of ion A^- is given by

$$c = 2[A_2B] + 2[B^{++}] + 2[AB^+] \quad (14)$$

Relative concentrations are defined by the equations

$$c\gamma_1 = [A^-], c\gamma_2 = [B^{++}], c\gamma_3 = [AB^+] \quad (15)$$

$$[A_2B] = c(1 - 2\gamma_2 - 2\gamma_3)/2 \quad (16)$$

The condition of electrical neutrality gives

$$\gamma_1 = 2\gamma_2 + \gamma_3 \quad (17)$$

If we approximate f_{A_2B} by unity and set off $f_A = f_{AB} = f$, the mass action equations become

$$k_1 = 2c\gamma_1\gamma_3 f^2/(1 - 2\gamma_2 - 2\gamma_3) \quad (18)$$

$$k_2 = c\gamma_1(\gamma_1 - \gamma_3)/f_B/2\gamma_3 \quad (19)$$

Experimental evidence on other quaternary salts²⁶ shows that 1-1 electrolytes of this type are only slightly associated in solvents of moderately high dielectric constant. As a working hypothesis, therefore, we shall assume that Reaction (10) is negligible, *i.e.* $[A_2B] = 0$ or $k_1 = \infty$. This leads to the relation

$$\gamma_3 = 1 - \gamma_1 \quad (20)$$

which, with (17), permits us to express γ_2 and γ_3 in terms of γ_1 .

(26) R. M. Fuoss and C. A. Kraus, *This Journal*, **55**, 1019 (1938).

If λ_j denotes the equivalent concentration of species j , then

$$\Lambda = \gamma_1\lambda_1 + 2\gamma_2\lambda_2 + \gamma_3\lambda_3 \quad (21)$$

At zero concentration, $\gamma_1 = 1$, $\gamma_2 = 1/2$ and $\gamma_3 = 0$. At a finite concentration

$$\lambda_j = \lambda_j^0 - \alpha_j\sqrt{c} \quad (22)$$

because mobility is decreased by electrostatic forces between ions. Substitution of (22) into (21) leads to a quite complicated expression; a fair approximation to the interionic terms can be made by lumping them all together, in the form

$$\Lambda = (\gamma_1\lambda_1^0 + 2\gamma_2\lambda_2^0 + \gamma_3\lambda_3^0)(1 - \delta\sqrt{c}) \quad (23)$$

where δ is the Onsager coefficient for a 2-1 salt, divided by Λ_0 . As dilution increases, γ_3 approaches zero and the ionic concentration approaches the total concentration, so the approximation is correct in the limit. At finite concentrations, the coefficient δ is of course a function of concentration, because the valence type is changing from 1-1 to 2-1 as Reaction (9) proceeds to the left.

If we eliminate γ_2 and γ_3 , and set $\lambda_3^0 = \lambda_2^0/2$ (because AB^+ is about the same size as B^{++} , but has only half the charge), Eq. (23) may be rearranged to

$$\begin{aligned} \gamma_1 &= \frac{\Lambda}{\Lambda_0} \left(\frac{1}{1 + \lambda_2^0/2\Lambda_0} \right) \left(\frac{1}{1 - \delta\sqrt{c}} + \frac{\lambda_2^0}{2\Lambda} \right) \quad (24) \\ &= (\Lambda/\Lambda_0) F(c, \Lambda_0) \quad (25) \end{aligned}$$

where F is a function which approximately corrects the conductance ratio Λ/Λ_0 for the effect of interionic forces on mobility. Using a preliminary extrapolation for Λ_0 and Hartley's value for λ_1^0 , $F(c, \Lambda_0)$ may be computed at each point; $F(0, \Lambda_0) = 1$ in the limit.

In order to calculate k_2 by means of Eq. (19), we also need a value for f_B . We shall use the Debye-Hückel first approximation

$$-\log f = 250.3 z_B^2 \sqrt{3c}/D^{3/2}$$

where z_B is 2 and $3c$ is the ional²⁷ concentration. In methanol at 25°

$$-\log f_B = 9.81\sqrt{c}$$

We realize the dilemma in regard to using a single ion activity coefficient but can offer no better suggestion than the one proposed. As in the mobility correction, we are again approximating ion concentration by total concentration and disregarding change of valence type with dilution.

A typical calculation is summarized in Fig. 3 for Salt III in ethanol (Series 1). A preliminary extrapolation gave $\Lambda_0 = 55.0$. Using this, and Hartley's value λ_0 (Br' in EtOH) = 25.8, values of $F(c, \Lambda_0)$ were computed. If we set

$$\begin{aligned} \Lambda' &= \Lambda F \\ c' &= cf_B \end{aligned}$$

the mass action equation for Reaction (10)

$$cf_B\gamma_1(\gamma_1 - 0.5)/(1 - \gamma_1) = k_2 \quad (19')$$

(27) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 33, Eq. 3-1-3.

may be rearranged to

$$\Lambda' = \Lambda_0 - [c'\Delta'(\Lambda' - \Lambda_0/2)]/k_2\Delta_0 \quad (26)$$

$$= \Lambda_0 - x/k_2\Delta_0 \quad (27)$$

According to Eq. (27), a plot of Λ' against x should be linear, with intercept Λ_0 at $c = 0$ and slope $1/k_2\Delta_0$. As will be seen in Fig. 3, the data at low concentrations give points which lie on a straight line. Similar calculations were made for Salt III in methanol and the methanol-ethanol mixture. For the latter, we interpolated λ_1^0 products on a viscosity scale to obtain $\lambda_1^0 = 42.4$ for the calculation of F .

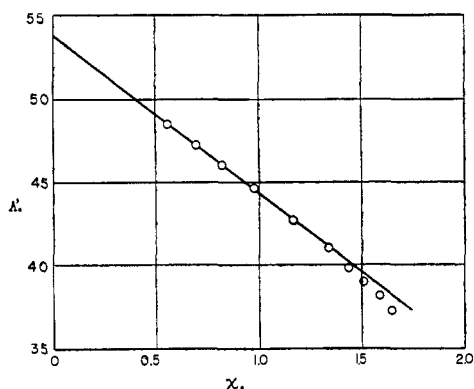


Fig. 3.—Salt III in ethanol, Eq. (27).

Having determined Λ_0 , the method and data may be tested in another way. It will be noted that Eq. (19') is extremely sensitive to the value chosen for Λ_0 , if the equation is used to compute k_2 , because the denominator is the difference between unity and a quantity which approaches unity in the limit. In Fig. 4, we show plots of

$$y = (1 - \gamma_1)/f_B\gamma_1(\gamma_1 - 0.5) \quad (28)$$

against c , where γ_1 was computed using the final values of Λ_0 obtained by the method of Fig. 3. It will be seen that the points lie on a straight line through the origin as required by Eq. (19). The slope is, of course, $1/k_2$.

Constants and limiting conductances for Salt III are summarized in Table IV. The magnitude

TABLE IV

Solvent	PROPERTIES OF SALT III				
	100 η	D	Λ_0	10^3k_2	10^3a
MeOH	0.5465	31.5	121.3	4.4 ₅	7.73
Mixt.	0.6868	28.0	92.1	1.7 ₇	6.30
EtOH	1.1047	24.3	53.6	0.20	4.25

of the dissociation constants is consistent with observations on other electrolytes. For spherical ions, with valences z_1 and z_2 , we have the relationship²⁶

$$K^{-1} = (4\pi N/1000)(z_1z_2e^2/DkT)^3Q(b) \quad (29)$$

where

$$b = z_1z_2e^2/aDkT, \quad (30)$$

a is "ionic diameter" or distance of closest approach, and $Q(b)$ is a function which has been tabulated by Bjerrum²⁶ for the range $2 \leq b \leq 15$ and by Fuoss and Kraus²⁶ for $15 \leq b \leq 80$. (Bjerrum's value for $Q(5)$ is in error; $Q(5) = 0.771$.) If we assume

(28) N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

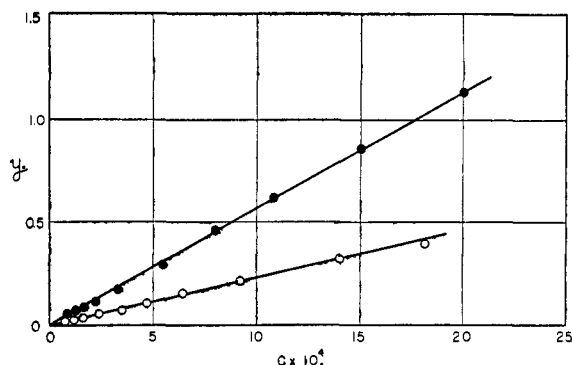


Fig. 4.—Salt IV in methanol (open circles) and in mixed solvent (solid circles), Eq. (28).

spherical ions, we would expect a 2-1 salt in ethanol to have about the same dissociation constant as a 1-1 salt in a solvent of half the dielectric constant, provided the ion sizes were equal. For tetrabutylammonium picrate in ethylene dichloride, where $D = 10.23$, Kraus²⁴ reports $K = 0.228 \times 10^{-3}$, which compares favorably with our value of 0.20×10^{-3} for Salt III in ethanol. Actually, of course, the cation of Salt III has anything but a central symmetry of charge; the effect of the asymmetry is best illustrated by calculating a values from the k_2 values of Table IV, using Eq. (29). These values are given in the last column of the table; a steady trend to larger values with increasing dielectric constant appears. If we use $a = 4.25 \times 10^{-8}$ and compute k_2 for methanol, we find 13.1×10^{-3} , compared to 4.45×10^{-3} observed. In other words, the salt is weaker in methanol than one would predict on the basis of the ethanol result and a spherical model. In order to make the calculation properly, we need the analog of Eq. (29), where the model is a pair of charges, separated by a (flexible) rod. The agreement in order of magnitude with the oversimplified model, however, supports the hypothesis that the properties of these electrolytes may be accounted for in terms of structure and electrostatic forces.

Summary

1. The conductances of dimethyl-di- β -ethanolammonium bromide (Salt I), dimethyl-di- β -acetoxyethanolammonium bromide (Salt II) and di-(β -trimethylammonium-ethyl) succinate dibromide (Salt III) have been measured in methanol. Salt III was also studied in ethanol and in a methanol-ethanol mixture of dielectric constant 28.0.

2. Salts I and II show slight association in methanol; $K = 0.03$ and 0.09 , respectively; Salt II is stronger than Salt I because the acetoxy groups in the cations decrease the attraction for the anion.

3. Salt III shows a fairly high degree of association of the second anion to the divalent cation; $k_2 = 4.5 \times 10^{-3}$ in methanol.

4. A method of obtaining Λ_0 and k_2 for 2-1 electrolytes in solvents of intermediate dielectric constant is described. It is essentially a modification of the Ostwald dilution law.